CBSE Class 12 Chemistry Question Paper 2014 with Solution PDF-Set 56/2 (Delhi)

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) All questions are compulsory.
(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vi) Use Log Tables, if necessary. Use of calculators is not allowed.

1. Give one example each of sol and gel. [1 mark]

Solution:

Concept:

- A sol has a solid dispersed phase in a liquid dispersion medium.
- A gel has a liquid dispersed phase in a solid dispersion medium.

Step 1: Identify a sol Paint is a sol: fine solid pigment particles are dispersed throughout a liquid medium. The particles form the dispersed phase, while the liquid forms the continuous dispersion medium.

Step 2: Identify a gel Jelly is a gel: liquid is held within a continuous solid network. Thus its dispersed phase is liquid and its dispersion medium is solid, reversing the phase combination found in a sol.

Step 3: Conclusion Sol: paint. Gel: jelly.

Quick Tip to Solve: For sol versus gel, first identify which phase forms the continuous medium.

2. Which reducing agent is employed to get copper from the leached low grade copper ore? [1 mark]

Solution:

Concept:

- A more reactive metal can reduce dissolved copper ions to copper metal.
- Iron supplies electrons: $\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-}$.

Step 1: Choose the reducing metal Scrap iron is employed to recover copper from the leached solution of low-grade copper ore. Iron is more reactive than copper and therefore displaces copper from its dissolved salt.

Step 2: Write the displacement reaction The ionic reaction is

$$\mathrm{Fe(s)} + \mathrm{Cu}^{2+}\mathrm{(aq)} \rightarrow \mathrm{Fe}^{2+}\mathrm{(aq)} + \mathrm{Cu(s)}.$$

Iron is oxidised and copper ions are reduced; consequently iron is the reducing agent.

Step 3: Conclusion The reducing agent is scrap iron, Fe.

Quick Tip to Solve: In copper recovery by displacement, the metal that dissolves supplies the electrons.

3. Write the IUPAC name of the compound $\mathrm{CH_3 - CH(NH_2) - CH_2 - CHO}$**.** [1 mark]

Solution:

Concept:

- The aldehyde group has priority over the amino group and supplies the suffix -al.
- Number the longest chain containing $-\mathrm{CHO}$ from the aldehyde carbon, which is carbon 1.

Step 1: Select and number the parent chain The structure is $\mathrm{CH_3 - CH(NH_2) - CH_2 - CHO}$. Its

Quick Tip to Solve: Count the aldehyde carbon as carbon 1 before locating the amino substituent.

parent chain contains four carbon atoms, including the aldehyde carbon. Numbering from $-CHO$ gives the parent name butanal.

Step 2: Locate the amino substituent The carbon adjacent to the aldehyde is carbon 2, and the carbon bearing $-NH_2$ is carbon 3. Since the aldehyde is the principal functional group, $-NH_2$ is named using the prefix amino with locant 3.

Step 3: Conclusion The IUPAC name is 3-aminobutanal.

Quick Tip to Solve: Count the aldehyde carbon as carbon 1 before locating the amino substituent.

4. Which of the following isomers is more volatile: o-nitrophenol or p-nitrophenol? [1 mark]

Solution:

Concept:

- Volatility increases when intermolecular attraction decreases.
- Intramolecular hydrogen bonding occurs within one molecule; intermolecular hydrogen bonding associates different molecules.

Step 1: Compare hydrogen bonding In o-nitrophenol, the neighbouring hydroxyl and nitro groups form an intramolecular hydrogen bond. In p-nitrophenol, their separation prevents this internal bond, and intermolecular hydrogen bonding occurs instead.

Step 2: Relate association to volatility Intermolecular hydrogen bonds associate p-nitrophenol molecules and require more energy to overcome during vaporisation. The reduced intermolecular association of o-nitrophenol allows it to vaporise more readily.

Step 3: Conclusion o-Nitrophenol is more volatile than p-nitrophenol.

Quick Tip to Solve: For the ortho isomer, check whether neighbouring groups can hydrogen-bond internally.

5. Some liquids on mixing form 'azeotropes'. What are 'azeotropes'? [1 mark]

Solution:

Concept:

- At a fixed pressure, an azeotrope boils at a constant temperature.
- The liquid and its equilibrium vapour have the same composition at the azeotropic composition.

Step 1: State the defining property Azeotropes are liquid mixtures that boil at a constant temperature and give vapour having the same composition as the boiling liquid. This behaviour occurs at a particular composition and specified pressure.

Step 2: Explain the consequence Because the escaping vapour has the same composition as the liquid, boiling does not enrich either component. Hence the components of an azeotrope cannot be separated by fractional distillation at that pressure.

Step 3: Conclusion Azeotropes are constant-boiling liquid mixtures whose vapour and liquid compositions are identical.

Quick Tip to Solve: Include both constant boiling and identical vapour-liquid composition in the definition.

6. Arrange the following compounds in increasing order of basicity:

$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$ [1 mark]

Solution:

Concept:

- An amine is more basic when the nitrogen lone pair is more available to accept a proton.
- Resonance delocalisation lowers lone-pair availability, whereas an alkyl group has an electron-releasing inductive effect.

Step 1: Compare the two aromatic amines In aniline, the nitrogen lone pair is delocalised into the benzene ring. N-Methylaniline also shows this delocalisation, but its methyl group releases electron density toward nitrogen, making it more basic than aniline.

Step 2: Compare benzylamine with aromatic amines In benzylamine, $C_6H_5CH_2NH_2$, the intervening $-CH_2-$ group prevents direct conjugation of the nitrogen lone pair with the benzene ring. Its lone pair is therefore more available for protonation than in either aromatic amine.

Step 3: Conclusion Increasing basicity:

$$C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2.$$

Quick Tip to Solve: Check whether nitrogen is directly bonded to the ring; a methylene spacer blocks conjugation.

7. Which component of starch is a branched polymer of α-glucose and insoluble in water? [1 mark]

Solution:

Concept:

- Starch contains two components, amylose and amylopectin, both built from α-glucose units.
- The presence of branch points distinguishes amylopectin from the essentially linear amylose component.

Step 1: Identify the branched component Amylopectin has glucose units joined mainly through $\alpha(1 \to 4)$ glycosidic bonds, with $\alpha(1 \to 6)$ glycosidic bonds at its branch points.

Step 2: Match the stated properties Amylopectin is the branched, water-insoluble component of starch. Amylose has an essentially unbranched chain and therefore does not match the branching specified in the question.

Step 3: Conclusion The component is $\boxed{\text{amylopectin}}$.

Quick Tip to Solve: Use the branch-point linkage: amylopectin has alpha(1 to 6) branching in addition to its main-chain links.

8. Which of the following is more stable complex and why?

$[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ [1 mark]

Solution:

Concept:

- The chelate effect makes a complex containing multidentate ligands more stable than a comparable complex containing only monodentate ligands.
- Ethylenediamine, en, is bidentate, whereas NH_3 is monodentate.

Step 1: Compare ligand attachment Each en ligand binds to cobalt through its two nitrogen donor atoms and forms a five-membered chelate ring. Three such ligands form three rings; ammonia forms no chelate ring.

Step 2: Apply the chelate effect Both complexes contain Co^{3+} with six nitrogen donor atoms. The greater stability of the ethylenediamine complex is attributed to chelation by the bidentate ligands.

Step 3: Conclusion $\boxed{[Co(en)_3]^{3+}}$ is more stable due to the chelate effect.

Quick Tip to Solve: When metal and coordination number are the same, check whether a ligand can form chelate rings.

9. State Henry's law. What is the effect of temperature on the solubility of a gas in a liquid? [2 marks]

Solution:

Concept:

- Henry's law relates the pressure of a gas above a solution to its mole fraction in that solution at a fixed temperature.
- Dissolution of gases in liquids is generally exothermic, so increasing temperature generally reduces their solubility.

Step 1: State Henry's law At constant temperature, the partial pressure p of a gas above a solution is directly proportional to its mole fraction x in the solution:

$$p = K_{\mathrm{H}} x.$$

Here K_{H} is the Henry's law constant for that gas in the specified solvent at that temperature. Thus at fixed temperature, raising the gas pressure raises its dissolved mole fraction.

Step 2: Explain the temperature effect The solubility of a gas in a liquid generally decreases with rise in temperature, at a fixed gas pressure. Gas dissolution is usually exothermic; added heat favours the reverse process, namely escape of dissolved gas into the gaseous phase. In terms of Henry's law, K_{H} generally rises with temperature, and therefore $x = p/K_{\mathrm{H}}$ falls at fixed p.

Step 3: Conclusion Henry's law is $p = K_{\mathrm{H}} x$ at fixed temperature; gas solubility generally decreases as temperature increases.

Quick Tip to Solve: Keep pressure fixed when discussing temperature: a larger Henry constant then means a smaller dissolved mole fraction.

10. Define the following terms:

(i) Pseudo first order reaction

(ii) Half life period of reaction ($t_{1/2}$) [2 marks]

Solution:

Concept:

- Reaction order describes the concentration dependence of the rate law; an effectively constant concentration may be absorbed into the rate constant.
- The half-life describes a specified change in the amount or concentration of a reactant, rather than the completion time of a reaction.

Step 1: Define pseudo first order reaction A reaction whose actual overall order is greater than one but which behaves kinetically as a first order reaction under specified conditions is called a pseudo first order reaction. This occurs when another reactant is present in such large excess that its concentration remains practically constant. For example, if $r = k[A][B]$ and $[B]$ is effectively constant, then $r = k_{\text{obs}}[A]$, where $k_{\text{obs}} = k[B]$.

Step 2: Define half-life period The half-life period, $t_{1/2}$, is the time required for the amount or concentration of a reactant to decrease to one-half of its initial value. Thus, starting from $[A]_0$, the concentration at $t = t_{1/2}$ is $[A]_0/2$. For a first order reaction specifically, $t_{1/2} = 0.693/k$; the definition itself applies to reactions of any order.

Step 3: Conclusion A pseudo first order reaction shows effective first order kinetics under the stated conditions; $t_{1/2}$ is the time for a reactant concentration to fall to half its initial value.

Quick Tip to Solve: For pseudo first order kinetics, name the excess reactant; for half-life, specify half of the initial reactant concentration.

11. Write the principle behind the following methods of refining:

(i) Hydraulic washing

(ii) Vapour phase refining [2 marks]

Solution:

Concept:

- Physical separation can exploit a difference in density between ore particles and the gangue accompanying them.
- Vapour phase refining requires selective formation of a volatile metal compound followed by its decomposition to regenerate the metal.

Step 1: Principle of hydraulic washing Hydraulic washing is based on the difference in densities of the ore and gangue particles. A current of water is passed over the powdered ore. The lighter gangue particles are carried away by the flowing water, while the heavier ore particles settle and remain behind. This operation concentrates the ore by gravity separation.

Step 2: Principle of vapour phase refining The impure metal is converted into a volatile compound

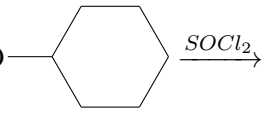
Quick Tip to Solve: For vapour phase refining, state both stages: make the metal volatile, then decompose the compound to recover pure metal.

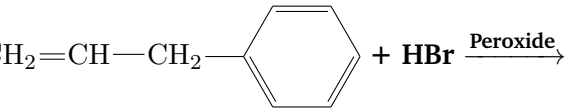
using a suitable reagent. The volatile compound is separated from the nonvolatile impurities and then decomposed under appropriate conditions to obtain pure metal. Thus the essential requirements are that the metal should form a volatile compound and that this compound should be readily decomposable to recover the metal. For example, nickel can form volatile $Ni(CO)_4$, which decomposes on heating to deposit pure nickel.

Step 3: Conclusion Hydraulic washing uses density differences; vapour phase refining uses formation, separation and decomposition of a volatile metal compound.

Quick Tip to Solve: For vapour phase refining, state both stages: make the metal volatile, then decompose the compound to recover pure metal.

12. Draw the structure of major monohalo product in each of the following reactions:

(i) 

(ii)  [2 marks]

Solution:

Concept:

- Thionyl chloride, $SOCl_2$, replaces the hydroxyl group of an alcohol by chlorine without changing its carbon skeleton.
- In the presence of peroxide, HBr adds to an unsymmetrical alkene by a radical mechanism: bromine attaches to the less substituted carbon of the double bond.

Step 1: (i) Replace the hydroxyl group of cyclohexanol The carbon bonded to OH in the six-membered ring becomes bonded to Cl. Thus cyclohexanol gives chlorocyclohexane (cyclohexyl chloride). The reaction is

$$C_6H_{11}OH + SOCl_2 \longrightarrow C_6H_{11}Cl + SO_2 + HCl.$$

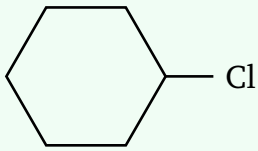
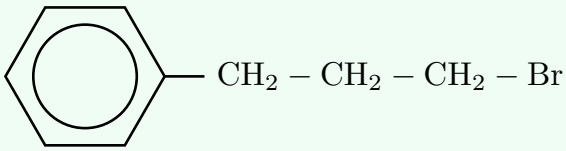
No double bond is introduced into the ring: this is replacement of OH by Cl.

Step 2: (ii) Apply the peroxide effect to the side-chain double bond The starting alkene is $C_6H_5CH_2CH{=}CH_2$. A bromine radical adds to its terminal carbon, giving the more stable secondary radical on the middle carbon. This radical abstracts hydrogen from HBr. Hence the net addition is anti-Markovnikov:

$$C_6H_5CH_2CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} C_6H_5CH_2CH_2CH_2Br.$$

The benzene ring remains unchanged; bromine enters the side chain at the terminal carbon.

Quick Tip to Solve: With SOCl2 replace only OH by Cl; with HBr/peroxide put Br on the terminal alkene carbon.

(i)  (ii) 

Structures of the two major monohalo products

Step 3: Conclusion The major products are (i) chlorocyclohexane and (ii) $C_6H_5CH_2CH_2CH_2Br$, 1-bromo-3-phenylpropane. Their structures are shown above.

Quick Tip to Solve: With SOCl2 replace only OH by Cl; with HBr/peroxide put Br on the terminal alkene carbon.

13. (i) Which alkyl halide from the following pair is chiral and undergoes faster S_N2 reaction?

(a) $CH_3CH_2CH_2CH_2Br$ **(b)** $CH_3CH(Br)CH_2CH_3$

(ii) Out of S_N1 and S_N2, which reaction occurs with

(a) Inversion of configuration

(b) Racemisation [2 marks]

Solution:

Concept:

- A tetrahedral carbon is a stereogenic centre when it is attached to four different groups; an alkyl halide containing one such centre is chiral.
- The bimolecular substitution mechanism, S_N2, requires backside attack and is favoured by low steric hindrance. The unimolecular mechanism, S_N1, passes through a planar carbocation.

Step 1: (i) Identify the chiral member and the faster reacting member In (b), 2-bromobutane, the carbon bearing Br is attached to Br, H, CH_3 and CH_2CH_3. These four different groups make this carbon stereogenic, so (b) is chiral. In (a), 1-bromobutane, the carbon bearing Br is a CH_2 carbon and has two identical hydrogen atoms, so it is achiral. For the faster S_N2 reaction, the answer is (a): its primary carbon offers less steric obstruction to an incoming nucleophile than the secondary carbon in (b). Thus the chiral member and the faster S_N2 substrate are different members of the pair.

Step 2: (ii) Connect the mechanism with stereochemical change (a) S_N2 occurs with inversion of configuration because the nucleophile attacks from the side opposite the leaving group in a single concerted step. (b) S_N1 occurs with racemisation because loss of the leaving group forms a planar carbocation. The nucleophile can attack either face, giving both configurations at the reaction centre.

Step 3: Conclusion (i) (b), 2-bromobutane, is chiral; (a), 1-bromobutane, undergoes faster S_N2 reaction. (ii) Inversion: S_N2; racemisation: S_N1.

Quick Tip to Solve: Test four groups for chirality, then separately compare steric crowding for SN2 speed.

14(a). Complete the following chemical equations:

(i) Ca_3P_2 + H_2O →

(ii) Cu + H_2SO_4(conc.) → [2 marks]

Solution:

Concept:

- Hydrolysis of a metal phosphide produces phosphine, PH_3, and the corresponding metal hydroxide.
- Concentrated sulphuric acid acts as an oxidising agent towards copper: copper is oxidised to the +2 state and sulphur is reduced from +6 to +4.

Step 1: (i) Hydrolyse calcium phosphide and balance the products The products are calcium hydroxide and phosphine. Three calcium atoms require three formula units of $Ca(OH)_2$, while two phosphorus atoms require two molecules of PH_3. Six water molecules supply the required oxygen and hydrogen:

$$\boxed{Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3}.$$

Both sides contain 3 Ca, 2 P, 6 O and 12 H atoms.

Step 2: (ii) Write the oxidation of copper by concentrated acid Copper forms copper(II) sulphate, while concentrated sulphuric acid is reduced to sulphur dioxide. Water is the other product:

$$\boxed{Cu + 2H_2SO_4(\text{conc.}) \xrightarrow{\text{heat}} CuSO_4 + SO_2 + 2H_2O}.$$

Copper loses two electrons, changing from 0 to +2; the sulphur atom reduced to SO_2 gains two electrons, changing from +6 to +4. The second sulphur atom remains as sulphate. Therefore two molecules of acid are required, and hydrogen gas is not a product.

Step 3: Conclusion The balanced equations are:

$$\text{(i)} \quad Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3.$$

$$\text{(ii)} \quad Cu + 2H_2SO_4(\text{conc.}) \rightarrow CuSO_4 + SO_2 + 2H_2O.$$

The second reaction occurs on heating.

Quick Tip to Solve: Phosphide plus water gives PH3; copper with concentrated sulphuric acid gives SO2, not hydrogen.

OR

14(b). Arrange the following in the order of property indicated against each set:

(i) HF, HCl, HBr, HI – increasing bond dissociation enthalpy.

(ii) H_2O, H_2S, H_2Se, H_2Te – increasing acidic character. [2 marks]

Solution:

Concept:

- Bond dissociation enthalpy is the energy required to break one mole of a specified bond in the gaseous state. Shorter hydrogen-halogen bonds are stronger.
- For group 16 hydrides, acidity increases as the H–E bond becomes weaker down the group, making release of a proton easier.

Step 1: (i) Compare hydrogen-halogen bond strengths From fluorine to iodine, the halogen atom becomes larger. The H–X bond becomes longer and orbital overlap becomes less effective, so the energy needed to break the bond decreases down the group. Hence the required increasing order is

$$\mathrm{HI} < \mathrm{HBr} < \mathrm{HCl} < \mathrm{HF}.$$

HF has the shortest and strongest bond; HI has the longest and weakest bond.

Step 2: (ii) Compare the acidic character of group 16 hydrides As the central atom changes from O to Te, its size increases and the H–E bond weakens. The hydride therefore loses a proton more readily down the group. The bond-strength effect governs this trend, giving

$$\mathrm{H_2O} < \mathrm{H_2S} < \mathrm{H_2Se} < \mathrm{H_2Te}.$$

Water is the least acidic member of this set.

Step 3: Conclusion (i) Bond dissociation enthalpy: $\mathrm{HI} < \mathrm{HBr} < \mathrm{HCl} < \mathrm{HF}$. (ii) Acidic character: $\mathrm{H_2O} < \mathrm{H_2S} < \mathrm{H_2Se} < \mathrm{H_2Te}$.

Quick Tip to Solve: Write both sequences from weakest property to strongest: HI starts the bond-energy order, while water starts the acidity order.

15. Write the IUPAC name of the complex $[Cr(NH_3)_4Cl_2]^+$. What type of isomerism does it exhibit? [2 marks]

Solution:

Concept:

- In coordination nomenclature, ligand names precede the metal name in alphabetical order. The oxidation state of the metal is written in Roman numerals.
- An octahedral complex of the type $[MA_4B_2]$ can have adjacent or opposite B ligands, producing cis and trans geometrical isomers.

Step 1: Determine the metal oxidation state and name Let the oxidation state of chromium be x.

Quick Tip to Solve: For $[MA_4B_2]$, place the two B ligands next to each other for cis and opposite each other for trans.

Each ammine ligand, NH_3, is neutral and each chlorido ligand has charge -1. The complex has charge $+1$, so

$$x + 4(0) + 2(-1) = +1 \quad \Rightarrow \quad x = +3.$$

Four ammine ligands give tetraammine and two chlorido ligands give dichlorido. Ammine is listed before chlorido, ignoring the numerical prefixes. The name is tetraamminedichloridochromium(III) ion.

Step 2: Identify the isomerism There are six donor atoms around chromium, giving an octahedral arrangement. The two chlorido ligands may occupy adjacent positions at $90°$, forming the cis isomer, or opposite positions at $180°$, forming the trans isomer. These have identical bonding but different spatial arrangements, so the complex exhibits geometrical isomerism.

Step 3: Conclusion The IUPAC name is tetraamminedichloridochromium(III) ion. It exhibits geometrical (cis–trans) isomerism.

Quick Tip to Solve: For $[MA_4B_2]$, place the two B ligands next to each other for cis and opposite each other for trans.

16. An element with density 11.2 g cm^{-3} forms a f.c.c. lattice with edge length of 4 $\times$ 10^{-8} cm. Calculate the atomic mass of the element.

(Given: N_A = 6.022 $\times$ 10^{23} mol^{-1}) [2 marks]

Solution:

Concept:

- For a cubic unit cell, $\rho = ZM/(N_A a^3)$, where ρ is density, Z is the number of atoms per unit cell, M is molar mass, N_A is Avogadro's constant and a is the edge length.
- An f.c.c. unit cell contains $Z = 4$ atoms: the eight corners contribute one atom in total and the six face centres contribute three.

Step 1: Calculate the unit-cell volume The edge length is already in centimetres, matching the density in $\mathrm{g\,cm^{-3}}$, so no length conversion is necessary. The volume is

$$a^3 = (4 \times 10^{-8})^3 = 64 \times 10^{-24} = 6.4 \times 10^{-23}\,\mathrm{cm^3}.$$

Cubing the length requires cubing both its numerical factor and its power of ten.

Step 2: Obtain the molar mass Rearrange the density equation and substitute $Z = 4$:

$$\begin{aligned} M &= \frac{\rho a^3 N_A}{Z} \\ &= \frac{11.2 \times 6.4 \times 10^{-23} \times 6.022 \times 10^{23}}{4} \\ &= 107.91424\,\mathrm{g\,mol^{-1}}. \end{aligned}$$

The powers of ten cancel. Thus the mass of one mole of atoms is approximately $108\,\mathrm{g}$; correspondingly, the atomic mass is approximately $108\,\mathrm{u}$.

Quick Tip to Solve: For f.c.c. use four atoms per cell, and cube the entire edge length before substituting into the density formula.

Step 3: Conclusion The atomic mass of the element is approximately $108\,\mathrm{u}$ (molar mass $107.9\,\mathrm{g\,mol^{-1}}$).

Quick Tip to Solve: For f.c.c. use four atoms per cell, and cube the entire edge length before substituting into the density formula.

17. Examine the given defective crystal

A^+	B^-	A^+	B^-	A^+
B^-	0	B^-	A^+	B^-
A^+	B^-	A^+	0	A^+
B^-	A^+	B^-	A^+	B^-

Answer the following questions:

(i) What type of stoichiometric defect is shown by the crystal?

(ii) How is the density of the crystal affected by this defect?

(iii) What type of ionic substances show such defect? [2 marks]

Solution:

Concept:

- A Schottky defect consists of vacancies of equal numbers of cations and anions in an ionic crystal, preserving electrical neutrality and the cation-to-anion ratio.
- Density is mass per unit volume. Removing ions from their normal lattice sites decreases the mass while the crystal volume remains approximately unchanged.

Step 1: (i) Identify the vacancies The zero in the second row occupies a site that should contain A^+, while the zero in the third row occupies a site that should contain B^-. Thus one cation and one anion are missing from normal lattice sites. Equal positive and negative charges are removed, maintaining electrical neutrality and stoichiometry. This is a Schottky defect.

Step 2: (ii) State the effect on density The vacancies reduce the mass of material within the same approximate lattice volume. Since $\rho = m/V$, the density decreases. There is no compensating ion at an interstitial site in the displayed arrangement.

Step 3: (iii) State the substances that show this defect Schottky defects are characteristic of ionic solids whose cations and anions have comparable sizes and whose coordination numbers are high. Standard examples are NaCl, KCl and CsCl. Comparable ion sizes favour paired vacancies rather than displacement of a small cation into an interstitial space.

Step 4: Conclusion (i) Schottky defect. (ii) The density decreases. (iii) Ionic solids with similarly sized cations and anions and high coordination numbers, such as NaCl, KCl and CsCl.

Quick Tip to Solve: Check which charge belongs at each zero: one missing cation plus one missing anion identifies a Schottky pair.

18. Calculate the mass of compound (molar mass = 256 g mol^{-1}) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K (K_f = 5.12 K kg mol^{-1}). [2 marks]

Solution:

Concept:

- For a dilute solution of a non-volatile, non-electrolyte solute, freezing-point depression is $\Delta T_f = K_f m$, where m is molality in moles of solute per kilogram of solvent.
- If the solute has mass w and molar mass M, then its amount is w/M. The mass of solvent must be expressed in kilograms when using the given K_f.

Step 1: Calculate the required molality The depression is the positive decrease in the freezing point, so $\Delta T_f = 0.48\,\text{K}$. Therefore

$$m = \frac{\Delta T_f}{K_f} = \frac{0.48}{5.12} = 0.09375\,\text{mol kg}^{-1}.$$

The given compound is treated as a molecular solute without association or dissociation.

Step 2: Convert molality to the mass of solute The benzene mass is $75\,\text{g} = 0.075\,\text{kg}$. Thus

$$\begin{aligned} n &= m \times \text{mass of solvent in kg} \\ &= 0.09375 \times 0.075 = 0.00703125\,\text{mol}, \\ w &= nM = 0.00703125 \times 256 = 1.80\,\text{g}. \end{aligned}$$

The solvent mass, rather than the total solution mass, enters molality. As a check, this amount in $0.075\,\text{kg}$ of benzene reproduces the required depression.

Step 3: Conclusion The mass of compound to be dissolved is $\boxed{1.80\,\text{g}}$.

Quick Tip to Solve: Convert the benzene mass to kilograms before using $\Delta T_f = K_f m$; molality uses solvent mass.

19(a). Give the structures of A, B and C in the following reactions:

(i) $\text{CH}_3\text{Br} \xrightarrow{KCN} \text{A} \xrightarrow{LiAlH_4} \text{B} \xrightarrow[273\,K]{HNO_2} \text{C}$

(ii) $\text{CH}_3\text{COOH} \xrightarrow[\Delta]{NH_3} \text{A} \xrightarrow{Br_2+KOH} \text{B} \xrightarrow{CHCl_3+NaOH} \text{C}$ [3 marks]

Solution:

Concept:

- With KCN, an alkyl halide forms a nitrile through carbon attack; the nitrile carbon increases the carbon chain by one. LiAlH_4 reduces a nitrile to a primary amine.
- A primary aliphatic amine reacts with nitrous acid to form the corresponding alcohol. Hofmann bromamide degradation converts an amide into a primary amine with one fewer carbon atom.
- The carbylamine reaction of a primary amine with chloroform and alkali gives an isocyanide, $\text{R}-\text{N} \equiv \text{C}$.

Quick Tip to Solve: Track carbon atoms: cyanide substitution adds one carbon; Hofmann degradation removes the amide carbonyl carbon.

Step 1: Identify the products in sequence (i) Carbon attack by cyanide replaces bromide, so $A = CH_3C \equiv N$, ethanenitrile. Reduction gives $B = CH_3CH_2NH_2$, ethanamine. Nitrous acid at 273 K converts this aliphatic primary amine to ethanol:

$$CH_3Br + KCN \longrightarrow CH_3CN + KBr,$$
$$CH_3CN + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2NH_2,$$
$$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O.$$

Thus $C = CH_3CH_2OH$. The aliphatic diazonium intermediate is unstable and loses nitrogen.

Step 2: Identify the products in sequence (ii) Ethanoic acid first gives ammonium ethanoate with ammonia; heating removes water to form $A = CH_3CONH_2$, ethanamide. Hofmann degradation yields $B = CH_3NH_2$, methanamine. The carbylamine reaction then gives $C = CH_3N \equiv C$, methyl isocyanide:

$$CH_3COOH + NH_3 \xrightarrow{\Delta} CH_3CONH_2 + H_2O,$$
$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O,$$
$$CH_3NH_2 + CHCl_3 + 3NaOH \longrightarrow CH_3NC + 3NaCl + 3H_2O.$$

In the final product the methyl group is bonded to nitrogen, distinguishing an isocyanide from a nitrile.

Step 3: Conclusion (i) $A = CH_3CN,\ B = CH_3CH_2NH_2,\ C = CH_3CH_2OH.$
(ii) $A = CH_3CONH_2,\ B = CH_3NH_2,\ C = CH_3NC.$

Quick Tip to Solve: Track carbon atoms: cyanide substitution adds one carbon; Hofmann degradation removes the amide carbonyl carbon.

OR

19(b). How will you convert the following:

(i) Nitrobenzene into aniline

(ii) Ethanoic acid into methanamine

(iii) Aniline into N-phenylethanamide (Write the chemical equations involved.) [3 marks]

Solution:

Concept:

- Reduction changes an aromatic nitro group, $-NO_2$, into an amino group, $-NH_2$, while preserving the benzene ring.
- Hofmann bromamide degradation converts $RCONH_2$ into RNH_2, eliminating the carbonyl carbon. Acetylation replaces one amino hydrogen by CH_3CO-.

Step 1: Convert nitrobenzene into aniline Reduce nitrobenzene with tin and hydrochloric acid. The acidic medium gives anilinium salt; treatment with aqueous sodium hydroxide liberates aniline. The

Quick Tip to Solve: For ethanoic acid to methanamine, use the amide followed by Hofmann degradation to shorten the chain by one carbon.

net reduction and work-up may be represented as

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2 + 2H_2O,$$
$$C_6H_5NH_3Cl + NaOH \longrightarrow C_6H_5NH_2 + NaCl + H_2O.$$

The second equation explicitly shows the release of the free amine from its salt.

Step 2: Convert ethanoic acid into methanamine React the acid with ammonia to form ammonium ethanoate and heat to obtain ethanamide. Then use bromine and potassium hydroxide for Hofmann degradation:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4,$$
$$CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O,$$
$$CH_3CONH_2 + Br_2 + 4KOH \longrightarrow CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

This removes one carbon, giving the required one-carbon amine from the two-carbon acid.

Step 3: Convert aniline into N-phenylethanamide Acetylate aniline with ethanoic anhydride:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

The product is acetanilide, also called N-phenylethanamide. Acetylation occurs at nitrogen: one N–H hydrogen is replaced by an acetyl group; the phenyl group remains attached to nitrogen.

Step 4: Conclusion The required routes are nitrobenzene $\xrightarrow{Sn/HCl;\ then\ NaOH}$ aniline; ethanoic acid $\xrightarrow{NH_3,\Delta}$ ethanamide $\xrightarrow{Br_2/KOH}$ methanamine; and aniline $\xrightarrow{(CH_3CO)_2O}$ $C_6H_5NHCOCH_3$.

Quick Tip to Solve: For ethanoic acid to methanamine, use the amide followed by Hofmann degradation to shorten the chain by one carbon.

20. (a) Write the mechanism of the following reaction:

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

(b) Write the equation involved in Reimer-Tiemann reaction. [3 marks]

Solution:

Concept:

- In reaction with hydrogen bromide, protonation converts the poor leaving group $-OH$ of an alcohol into water, a good leaving group.
- Ethanol is a primary alcohol; bromide ion substitutes by an S_N2 attack on the carbon bonded to oxygen, without a free primary carbocation.
- The Reimer-Tiemann reaction introduces a formyl group $-CHO$ mainly at the ortho position of phenol using chloroform and aqueous sodium hydroxide, followed by acidification.

Step 1: (a) Protonate ethanol Oxygen of ethanol donates a lone pair to a proton from HBr, producing

Quick Tip to Solve: For a primary alcohol with HBr, protonate OH first and show direct bromide displacement; for Reimer-Tiemann, place CHO ortho to phenolic OH.

protonated ethanol and bromide ion:

$$CH_3CH_2OH + HBr \rightleftharpoons CH_3CH_2OH_2^+ + Br^-.$$

This activation is essential because direct loss of hydroxide ion from ethanol is unfavourable, whereas neutral water can leave readily.

Step 2: (a) Displace water with bromide Bromide ion attacks the primary carbon from the side opposite the carbon-oxygen bond. Formation of the carbon-bromine bond and breaking of the carbon-oxygen bond occur together:

$$Br^- + CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2Br + H_2O.$$

The electron pair of the carbon-oxygen bond goes to oxygen as water departs. Thus the mechanism is nucleophilic substitution, with no separate ethyl carbocation intermediate.

Step 3: (b) Write the Reimer-Tiemann equation Phenol is heated with chloroform and aqueous sodium hydroxide; acidification gives salicylaldehyde (2-hydroxybenzaldehyde) as the major product. The balanced equation, showing the neutral organic product after work-up, is

$$C_6H_5OH + CHCl_3 + 3NaOH \xrightarrow[\text{then } H^+]{\Delta} \text{o–}\ HOC_6H_4CHO + 3NaCl + 2H_2O.$$

A small amount of the para isomer may also form; the characteristic major product is the ortho aldehyde.

Step 4: Conclusion (a) Ethanol undergoes protonation followed by S_N2 displacement of water by Br^-, giving bromoethane. (b) Phenol with $CHCl_3/NaOH$, followed by acidification, gives mainly salicylaldehyde.

Quick Tip to Solve: For a primary alcohol with HBr, protonate OH first and show direct bromide displacement; for Reimer-Tiemann, place CHO ortho to phenolic OH.

21. After the ban on plastic bags, students of one school decided to make the people aware of the harmful effects of plastic bags on environment and Yamuna River. To make the awareness more impactful, they organized rally by joining hands with other schools and distributed paper bags to vegetable vendors, shopkeepers and departmental stores. All students pledged not to use polythene bags in future to save Yamuna River.

After reading the above passage, answer the following questions:

(i) What values are shown by the students?

(ii) What are biodegradable polymers? Give one example.

(iii) Is polythene a condensation or an addition polymer? [3 marks]

Solution:

Concept:

- Environmental responsibility means recognising the effects of human activities on ecosystems and taking practical action to reduce pollution.
- Biodegradable polymers can be broken down by biological processes, especially the enzymatic action of microorganisms, into simpler substances.
- Addition polymerisation joins unsaturated monomers by opening their multiple bonds, without eliminating small molecules such as water.

Step 1: (i) Identify the values demonstrated The students show environmental awareness and concern for the protection of the Yamuna River. Their rally and distribution of paper bags demonstrate social responsibility, initiative and a willingness to turn awareness into practical action. Joining hands with other schools shows cooperation and teamwork. Their pledge to stop using polythene bags shows commitment to conserving the environment and encouraging responsible habits in the community.

Step 2: (ii) Define biodegradable polymers and give an example Biodegradable polymers are polymers which undergo degradation by microorganisms, such as bacteria, through biological or enzymatic action, yielding simpler products. Their chains contain linkages that can be broken down under suitable biological conditions. One example is PHBV, poly(β-hydroxybutyrate-co-β-hydroxyvalerate), a biodegradable copolyester. Its ester linkages allow biological degradation. Thus it differs from persistent conventional polythene, whose carbon-carbon backbone resists such breakdown.

Step 3: (iii) Classify polythene Polythene is an addition polymer of ethene. The carbon-carbon double bonds in ethene open and the monomers join to form a long chain:

$$n\,CH_2{=}CH_2 \longrightarrow [-CH_2 - CH_2-]_n\,.$$

No water, hydrogen chloride or other small molecule is eliminated in this process. Therefore it is addition polymerisation, whereas condensation polymerisation involves the repeated joining of suitable functional groups, usually with elimination of small molecules.

Step 4: Conclusion (i) The students show environmental concern, social responsibility, cooperation and commitment. (ii) Biodegradable polymers are broken down biologically; PHBV is an example. (iii) Polythene is an addition polymer.

Quick Tip to Solve: Trace polythene back to ethene: opening C=C without loss of a small molecule identifies addition polymerisation immediately.

22. (a) Draw the structures of the following molecules:

(i) XeF_2

(ii) BrF_3

(b) Write the structural difference between white phosphorus and red phosphorus. [3 marks]

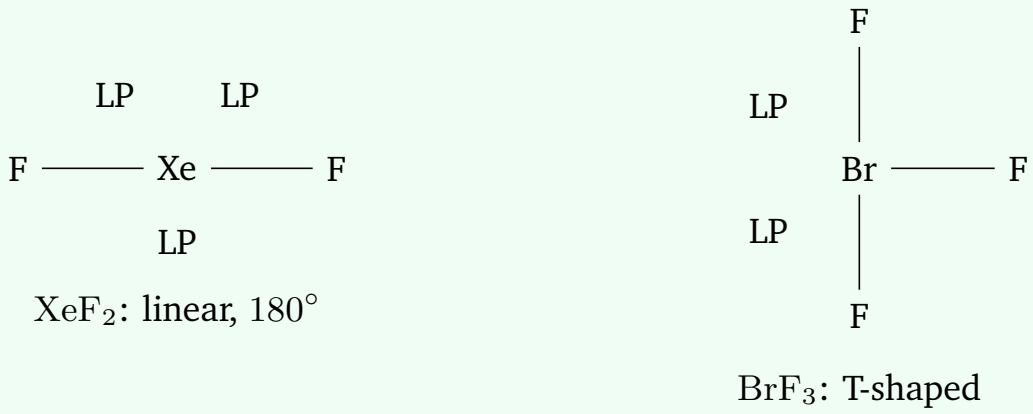
Solution:

Concept:

- Valence-shell electron-pair repulsion (VSEPR) theory determines molecular shape from bond pairs and lone pairs on the central atom. Lone pairs occupy equatorial positions preferentially in a trigonal-bipyramidal electron-pair arrangement.
- White phosphorus contains discrete tetrahedral P_4 molecules; red phosphorus has an extended polymeric structure joined by covalent bonds.

Step 1: (a)(i) Structure of xenon difluoride Xenon has eight valence electrons. In XeF_2, two pairs form Xe–F bonds and three pairs remain as lone pairs on Xe. Thus it is an AX_2E_3 species with five electron-pair domains. All three lone pairs occupy the equatorial positions of the trigonal bipyramid, leaving the two fluorine atoms in opposite axial positions. The molecular shape is linear, with $\angle F - Xe - F = 180°$.

Step 2: (a)(ii) Structure of bromine trifluoride Bromine has seven valence electrons. Three bond pairs and two lone pairs surround Br in BrF_3, so it is an AX_3E_2 species. The two lone pairs occupy equatorial positions; the fluorine atoms occupy two axial and one equatorial position. Consequently the molecule is T-shaped. Lone-pair repulsion slightly distorts the ideal $90°$ and $180°$ bond angles.



Molecular structures; LP denotes a lone pair on the central atom.

Step 3: (b) Structural difference between the phosphorus allotropes White phosphorus consists of separate tetrahedral P_4 molecules: each phosphorus atom is bonded to the other three atoms of the tetrahedron. Red phosphorus is polymeric, with linked phosphorus units forming an extended covalent network rather than separate P_4 molecules. The small bond angles in the white-phosphorus tetrahedron cause strain; the extended red-phosphorus structure has much less strain.

Step 4: Conclusion XeF_2 is linear and BrF_3 is T-shaped. White phosphorus is molecular (tetrahedral P_4); red phosphorus is polymeric.

Quick Tip to Solve: Count lone pairs first: Xe has three in XeF2, while Br has two in BrF3; place these equatorially before identifying the molecular shape.

23. (a) In reference to Freundlich adsorption isotherm write the expression for adsorption of gases on solids in the form of an equation.

(b) Write an important characteristic of lyophilic sols.

(c) Based on type of particles of dispersed phase, give one example each of associated colloid and multimolecular colloid. [3 marks]

Solution:

Concept:

- An adsorption isotherm relates the amount adsorbed per unit mass of adsorbent to the equilibrium pressure of a gas at a fixed temperature.
- Colloids may be classified by affinity for the dispersion medium or by the nature of the dispersed particles; these are different bases of classification.

Step 1: (a) Freundlich adsorption isotherm For adsorption of a gas on a solid at constant temperature, the empirical Freundlich equation is

$$\frac{x}{m} = kp^{1/n}, \qquad 0 < \frac{1}{n} < 1.$$

Here x is the mass of gas adsorbed, m is the mass of solid adsorbent and p is the equilibrium gas pressure. The constants k and n depend on the gas, adsorbent and temperature. Equivalently, $\log(x/m) = \log k + (1/n)\log p$. Thus adsorption increases with pressure in the range where this empirical relation applies.

Step 2: (b) Important characteristic of lyophilic sols Lyophilic sols are reversible: if the dispersion medium is removed, the sol can be formed again by adding the dispersion medium to the residue. Their dispersed particles have strong affinity for the medium and become extensively solvated, which also makes these sols relatively stable.

Step 3: (c) Examples based on the nature of dispersed particles An associated colloid is a soap solution above its critical micelle concentration (CMC). Soap molecules aggregate into micelles, with hydrophobic hydrocarbon chains directed inward and hydrophilic ionic groups toward water. A multimolecular colloid is a gold sol: many gold atoms aggregate to form each particle of colloidal size. Micelles arise by association of surfactant molecules, whereas gold-sol particles are aggregates of numerous small atoms.

Step 4: Conclusion $x/m = kp^{1/n}$ at constant temperature; lyophilic sols are reversible. Soap micelles exemplify associated colloids, and gold sol exemplifies multimolecular colloids.

Quick Tip to Solve: Keep the two classifications separate: reversibility describes lyophilic sols, while soap micelles and gold aggregates identify particle types.

24. Account for the following:

(i) Bi(V) is a stronger oxidizing agent than Sb(V).

(ii) N−N single bond is weaker than P−P single bond.

(iii) Noble gases have very low boiling points. [3 marks]

Solution:

Concept:

- The inert-pair effect is the increasing reluctance of the outermost ns^2 electron pair to participate in bonding down a heavy p-block group.
- An oxidizing agent accepts electrons and is reduced. Bond strength and boiling point depend on different interactions: intramolecular bonding and intermolecular attraction, respectively.

Step 1: (i) Compare the stability of oxidation states In group 15, the inert-pair effect increases from antimony to bismuth. Thus the $+3$ state is more stable relative to the $+5$ state for Bi than for Sb. Consequently, Bi(V) has a greater tendency to accept two electrons and change to Bi(III):

$$\mathrm{Bi(V)} + 2\mathrm{e}^- \longrightarrow \mathrm{Bi(III)}.$$

This greater tendency to undergo reduction makes Bi(V) a stronger oxidizing agent than Sb(V).

Step 2: (ii) Explain the weak nitrogen single bond Each nitrogen atom in an $\mathrm{N}-\mathrm{N}$ single bond has a lone pair. Nitrogen is very small, so the nonbonding electron pairs on adjacent nitrogen atoms are close together and strongly repel one another. This destabilizes the single bond. Phosphorus atoms are larger and their lone pairs are farther apart, giving less repulsion; therefore the $\mathrm{P}-\mathrm{P}$ single bond is stronger.

Step 3: (iii) Identify the forces between noble-gas atoms Noble gases exist as separate, electrically neutral monatomic particles with closed valence shells. Their atoms are held together only by weak London dispersion forces. Little thermal energy is needed to overcome these attractions and separate the atoms into the gas phase, so their boiling points are very low.

Step 4: Conclusion Bi(V) is the stronger oxidant because Bi(III) is stabilized by the inert-pair effect; strong lone-pair repulsion weakens $\mathrm{N}-\mathrm{N}$; weak dispersion attractions give noble gases low boiling points.

Quick Tip to Solve: For Bi compare oxidation-state stability; for N compare lone-pair repulsion; for boiling compare forces between particles.

25. (i) Name the sweetening agent used in the preparation of sweets for a diabetic patient.

(ii) What are antibiotics? Give an example.

(iii) Give two examples of macromolecules that are chosen as drug targets. [3 marks]

Solution:

Concept:

- Artificial sweeteners supply sweetness without using ordinary sucrose as the sweetening ingredient; saccharin is a standard example used for diabetic patients.
- Drugs act by interacting with biological macromolecules. Antibiotics inhibit susceptible microorganisms at low concentrations.

Step 1: (i) Name the sweetening agent **Saccharin** is used as an artificial sweetening agent in sweets prepared for a diabetic patient. It is intensely sweet and is excreted largely unchanged rather than being metabolized like ordinary sugar, so it supplies sweetness without the calorific contribution of sucrose. This is the relevant property for the requested example.

Step 2: (ii) Define antibiotics and give an example Antibiotics are chemical substances produced by microorganisms, or their synthetic and semisynthetic analogues, which in low concentrations kill other microorganisms or inhibit their growth by interfering with essential metabolic processes. **Penicillin** is an example. It acts against susceptible bacteria by interfering with bacterial cell-wall formation. Antibiotics are therefore distinguished by their antimicrobial action; the term does not mean any substance used to relieve pain or fever.

Step 3: (iii) Give two macromolecular drug targets Two examples are **proteins** and **nucleic acids**. Enzymes and receptor proteins are important protein targets: binding of a drug can alter enzyme activity or the response to a chemical messenger. Nucleic acids, such as DNA, can also be targets when a drug interferes with their replication or functioning. These are biological macromolecules with which a drug interacts to produce its effect.

Step 4: Conclusion (i) Saccharin. (ii) Antibiotics kill or inhibit microorganisms at low concentrations; example: penicillin. (iii) Proteins and nucleic acids.

Quick Tip to Solve: Remember the three distinct requests: a sweetener, an antibiotic definition plus example, and two classes of macromolecular targets.

26. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume:

$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$

Experiment	Time/s^{-1}	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

(Given: log 4 = 0.6021, log 2 = 0.3010) [3 marks]

Solution:

Concept:

- At constant temperature and volume, the partial pressure of a gas is proportional to its amount. Total pressure is the sum of the partial pressures.
- For a first-order reaction, $k = \dfrac{2.303}{t}\log\left(\dfrac{p_0}{p_A}\right)$, where p_0 and p_A are the initial and remaining reactant partial pressures.

Step 1: Relate decomposition to the total pressure Initially only SO_2Cl_2 is present, at $p_0 = 0.4$ atm. Let x atm be the pressure equivalent of reactant decomposed in 100 s. From

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g),$$

the partial pressures at that time are $0.4 - x$, x, and x, respectively. Each decomposed molecule produces two product molecules, so total pressure increases by x, rather than decreasing.

Step 2: Find the remaining reactant pressure The measured total pressure is 0.7 atm. Therefore

$$0.7 = (0.4 - x) + x + x = 0.4 + x,$$

giving $x = 0.3$ atm. Hence

$$p_A = 0.4 - 0.3 = 0.1 \text{ atm}.$$

Equivalently, $p_A = 2p_0 - P_t$. The total pressure 0.7 atm must not be substituted as the reactant pressure in the integrated rate law.

Step 3: Apply the first-order integrated rate law Using the elapsed time of 100 s and the supplied logarithm,

$$k = \frac{2.303}{100}\log 4 = \frac{2.303 \times 0.6021}{100} = 0.013866\,s^{-1}.$$

A first-order rate constant has units of inverse time. The reactant fraction remaining is $1/4$, consistent with two half-lives in the stated interval.

Step 4: Conclusion The rate constant is $\boxed{k = 1.39 \times 10^{-2}\,s^{-1}}$.

Quick Tip to Solve: For a gas decomposition A to B plus C, first compute the remaining reactant pressure as twice initial pressure minus total pressure.

27. (i) Deficiency of which vitamin causes rickets?

(ii) Give an example for each of fibrous protein and globular protein.

(iii) Write the product formed on reaction of D-glucose with Br_2 water. [3 marks]

Solution:

Concept:

- Vitamins are essential micronutrients; their deficiency causes characteristic disorders. Vitamin D supports calcium and phosphate absorption and normal mineralisation of bones.
- Fibrous proteins have extended, fibre-like structures, whereas globular proteins fold into compact shapes. Mild oxidation of an aldehyde converts its $-CHO$ group into $-COOH$.

Step 1: Identify the vitamin (i) Rickets is caused by deficiency of vitamin D. In children, inadequate vitamin D reduces normal calcium and phosphate availability for mineralisation, leaving growing bones soft and liable to bend.

Step 2: Give the two protein examples (ii) Keratin, present in hair and wool, is a fibrous protein: its extended chains form a strong structural material. Insulin is a globular protein: its polypeptide chains form a compact, biologically active structure. Thus keratin and insulin provide one example of each requested class.

Step 3: Identify the oxidation product (iii) Bromine water mildly oxidises the aldehydic group of the open-chain form of D-glucose to a carboxyl group. The terminal primary alcohol group remains unchanged. Hence the product is D-gluconic acid:

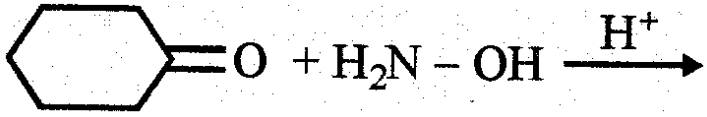
$$\mathrm{CHO(CHOH)_4CH_2OH + Br_2 + H_2O \longrightarrow COOH(CHOH)_4CH_2OH + 2HBr.}$$

This reaction establishes the presence of an aldehydic group in glucose; it does not oxidise both terminal groups to give a dicarboxylic acid.

Step 4: Conclusion (i) Vitamin D. (ii) Fibrous protein: keratin; globular protein: insulin. (iii) D-gluconic acid, $\mathrm{COOH(CHOH)_4CH_2OH}$.

Quick Tip to Solve: For bromine water and glucose, change only the aldehyde end to a carboxyl group; retain the terminal alcohol.

28(a). **Write the products of the following reactions:** [3 marks]

(i) 

(ii) $2\,C_6H_5CHO + \text{conc. } NaOH \longrightarrow$

(iii) $CH_3COOH \xrightarrow{Cl_2/P}$

Solution:

Concept:

- Hydroxylamine condenses with a carbonyl compound to give an oxime, replacing the carbonyl oxygen by $= N - OH$ with elimination of water.
- An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction in concentrated alkali. Carboxylic acids containing an alpha hydrogen undergo alpha halogenation with halogen and phosphorus.

Step 1: (i) Form the oxime of cyclohexanone The cyclic ketone reacts with hydroxylamine in the presence of acid. The ring remains intact, and its carbonyl group $> C = O$ changes into $> C = N - OH$. Thus the product is cyclohexanone oxime, accompanied by water:

$$\underset{\text{cyclohexanone}}{(CH_2)_5CO} + NH_2OH \xrightarrow{H^+} \underset{\text{cyclohexanone oxime}}{(CH_2)_5C{=}N{-}OH} + H_2O.$$

In these condensed formulae the five methylene groups and the carbonyl or oxime carbon form the six-membered ring.

Step 2: (ii) Apply the Cannizzaro reaction Benzaldehyde has no alpha hydrogen. In concentrated sodium hydroxide, two molecules undergo disproportionation: one aldehyde group is reduced to a primary alcohol, while the other is oxidised to the carboxylate salt. The products are benzyl alcohol and sodium benzoate:

$$2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa.$$

Sodium benzoate is written rather than free benzoic acid because the reaction medium is alkaline.

Step 3: (iii) Replace an alpha hydrogen by chlorine Chlorine in the presence of phosphorus gives the Hell-Volhard-Zelinsky reaction of ethanoic acid. One hydrogen on the carbon next to the carboxyl group is replaced by chlorine, giving chloroethanoic acid (chloroacetic acid):

$$CH_3COOH + Cl_2 \xrightarrow{P} ClCH_2COOH + HCl.$$

The carboxyl group is retained; substitution occurs at the alpha carbon.

Step 4: Conclusion (i) Cyclohexanone oxime, $(CH_2)_5C{=}N{-}OH$ (cyclic). (ii) Benzyl alcohol and sodium benzoate. (iii) Chloroethanoic acid, $ClCH_2COOH$.

Quick Tip to Solve: Match each reagent first: hydroxylamine gives an oxime, concentrated alkali gives Cannizzaro products, and chlorine/phosphorus chlorinates the alpha carbon.

28(b). Give simple chemical tests to distinguish between the following pairs of compounds:

(i) Benzaldehyde and Benzoic acid

(ii) Propanal and Propanone [2 marks]

Solution:

Concept:

- A carboxylic acid liberates carbon dioxide from sodium hydrogen carbonate; an aldehyde does not show this acid-base reaction.
- Tollens reagent is ammoniacal silver nitrate. Aldehydes reduce its silver(I) complex to metallic silver, whereas ordinary ketones do not.

Step 1: Distinguish benzaldehyde from benzoic acid (i) Add aqueous sodium hydrogen carbonate separately to the two samples. Benzoic acid gives brisk effervescence of carbon dioxide, while benzaldehyde gives no such effervescence. The positive reaction is

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2 \uparrow.$$

The evolved gas turns limewater milky, confirming carbon dioxide.

Step 2: Distinguish propanal from propanone (ii) Warm each sample gently with freshly prepared Tollens reagent. Propanal gives a silver mirror (or a deposit of metallic silver), while propanone gives no silver mirror. Propanal is oxidised to propanoate in the alkaline reagent:

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^-$$

$$\longrightarrow CH_3CH_2COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O.$$

Thus the observation directly identifies the aldehyde in the second pair.

Step 3: Conclusion (i) Aqueous $NaHCO_3$: benzoic acid effervesces; benzaldehyde does not. (ii) Tollens test: propanal gives a silver mirror; propanone does not.

Quick Tip to Solve: Use bicarbonate to identify the acid in the first pair and Tollens reagent to identify the aldehyde in the second.

OR

28(a). Account for the following:

(i) CH_3CHO is more reactive than CH_3COCH_3 towards reaction with HCN.

(ii) Carboxylic acid is a stronger acid than phenol. [2 marks]

Solution:

Concept:

- Addition of HCN to a carbonyl compound begins with nucleophilic attack of CN^- on the electrophilic carbonyl carbon. Electronic effects and steric hindrance control its ease.
- An acid is stronger when its conjugate base is more stable; resonance delocalisation stabilises both

Quick Tip to Solve: For carbonyl addition compare both methyl-group donation and crowding; for acidity compare where the conjugate base carries its negative charge.

carboxylate and phenoxide ions, but to different extents.

Step 1: (i) Compare the carbonyl compounds Ethanal, CH_3CHO, has one methyl group and one hydrogen attached to the carbonyl carbon, whereas propanone, CH_3COCH_3, has two methyl groups. The electron-releasing $+I$ effect of the second methyl group reduces the partial positive charge on the carbonyl carbon of propanone. Hence attack by CN^- is less favourable electronically. Its two methyl groups also cause greater steric hindrance to the approaching nucleophile. Ethanal therefore undergoes HCN addition more readily, forming $CH_3CH(OH)CN$.

Step 2: (ii) Compare the conjugate bases A carboxylic acid loses a proton to give $RCOO^-$. Its two equivalent resonance structures distribute the negative charge equally over two electronegative oxygen atoms. Phenol gives $C_6H_5O^-$, whose resonance structures are not equivalent: delocalisation into the ring places negative charge on carbon atoms, which are less electronegative than oxygen. Thus phenoxide is less effectively stabilised than carboxylate. Formation of the carboxylate ion is consequently more favourable, so carboxylic acids release H^+ more readily than phenol.

Step 3: Conclusion (i) Ethanal is more reactive towards HCN because it has a more electrophilic and less hindered carbonyl carbon. (ii) Carboxylic acids are stronger acids because their carboxylate conjugate bases have greater resonance stabilisation than phenoxide.

Quick Tip to Solve: For carbonyl addition compare both methyl-group donation and crowding; for acidity compare where the conjugate base carries its negative charge.

28(b). Write the chemical equations to illustrate the following name reactions:

(i) Wolff-Kishner reduction

(ii) Aldol condensation

(iii) Cannizzaro reaction [3 marks]

Solution:

Concept:

- Wolff-Kishner reduction replaces the carbonyl oxygen of an aldehyde or ketone by two hydrogen atoms, using hydrazine followed by heating with strong base.
- Aldol condensation requires an aldehyde or ketone with an α-hydrogen. Cannizzaro disproportionation is shown by aldehydes without an α-hydrogen in concentrated alkali.

Step 1: (i) Wolff-Kishner reduction Propanone reacts with hydrazine to form its hydrazone, which on heating with KOH in ethylene glycol gives propane with evolution of nitrogen. The overall equation is

$$CH_3COCH_3 + H_2NNH_2 \xrightarrow[\text{ethylene glycol, heat}]{\text{KOH}} CH_3CH_2CH_3 + N_2 + H_2O.$$

The carbon skeleton remains unchanged: only the carbonyl group is reduced to a methylene group.

Step 2: (ii) Aldol condensation Ethanal contains α-hydrogen atoms. In cold dilute NaOH, two

Quick Tip to Solve: Check for an alpha hydrogen before choosing aldol or Cannizzaro, and always show heat and strong base with hydrazine in Wolff-Kishner reduction.

molecules combine to give the aldol, 3-hydroxybutanal:

$$2CH_3CHO \xrightarrow[\text{cold}]{\text{dilute NaOH}} CH_3CH(OH)CH_2CHO.$$

On heating, the aldol loses water to form but-2-enal, an α,β-unsaturated aldehyde:

$$CH_3CH(OH)CH_2CHO \xrightarrow{\text{heat}} CH_3CH{=}CHCHO + H_2O.$$

Giving both equations distinguishes aldol formation from the subsequent dehydration that completes the condensation.

Step 3: (iii) Cannizzaro reaction Benzaldehyde has no α-hydrogen and undergoes disproportionation in concentrated NaOH:

$$2C_6H_5CHO + NaOH \xrightarrow{\text{concentrated alkali}} C_6H_5CH_2OH + C_6H_5COONa.$$

One aldehyde molecule is reduced to benzyl alcohol while the other is oxidised to sodium benzoate. The product in the alkaline reaction mixture is the carboxylate salt; free benzoic acid is obtained only after acidification.

Step 4: Conclusion The equations illustrate carbonyl reduction to propane, aldol condensation of ethanal to but-2-enal, and Cannizzaro disproportionation of benzaldehyde to benzyl alcohol and sodium benzoate, respectively.

Quick Tip to Solve: Check for an alpha hydrogen before choosing aldol or Cannizzaro, and always show heat and strong base with hydrazine in Wolff-Kishner reduction.

29(a). Define the following terms:

(i) Limiting molar conductivity

(ii) Fuel cell

(b) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 $\times$ 10^{-2} Ω^{-1} cm^{-1}. [5 marks]

Solution:

Concept:

- Molar conductivity, Λ_m, is the conductance of the volume of solution containing one mole of electrolyte, placed between electrodes one unit distance apart. Its limiting value at infinite dilution is denoted by Λ_m°.
- For a conductivity cell, $\kappa = G(l/A) = (l/A)/R$, where κ is conductivity, $G = 1/R$ is conductance and l/A is the cell constant. The same cell has the same cell constant for both solutions.
- If κ is in $S\,cm^{-1}$ and concentration c is in $mol\,L^{-1}$, then $\Lambda_m = 1000\kappa/c$ in $S\,cm^2\,mol^{-1}$.

Step 1: (a)(i) Define limiting molar conductivity Limiting molar conductivity is the molar conductivity

Quick Tip to Solve: For the same conductivity cell, first use $\kappa_1 R_1 = \kappa_2 R_2$; then multiply the new conductivity by $1000/c_2$ to obtain molar conductivity.

of an electrolyte when its concentration approaches zero, that is, at infinite dilution:

$$\Lambda_m^\circ = \lim_{c \to 0} \Lambda_m.$$

At this limit, ions are sufficiently far apart that interionic interactions become negligible and each ion contributes independently to the total molar conductivity. Its usual unit is $\mathrm{S\,cm^2\,mol^{-1}}$.

Step 2: (a)(ii) Define a fuel cell A fuel cell is a galvanic cell that converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy. The reactants are fed to the electrodes from outside, and products are removed, so the cell can operate as long as the reactants continue to be supplied. For example, a hydrogen-oxygen fuel cell uses hydrogen as fuel and oxygen as oxidant, with water as the product.

Step 3: (b) Determine the cell constant using the standard solution The conductivity of the $0.1\,\mathrm{mol\,L^{-1}}$ KCl solution is $\kappa_1 = 1.29 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$, and its resistance is $R_1 = 100\,\Omega$. Hence,

$$\frac{l}{A} = \kappa_1 R_1 = (1.29 \times 10^{-2})(100) = 1.29\,\mathrm{cm^{-1}}.$$

This geometrical constant is unchanged when the first solution is replaced by the second solution in the same cell.

Step 4: Calculate the conductivity of the dilute solution For the $0.02\,\mathrm{mol\,L^{-1}}$ KCl solution, $R_2 = 520\,\Omega$. Therefore,

$$\kappa_2 = \frac{l/A}{R_2} = \frac{1.29}{520} = 2.48077 \times 10^{-3}\,\mathrm{S\,cm^{-1}}.$$

The higher resistance corresponds to a smaller conductivity, as expected when the number of ions per unit volume is reduced by dilution.

Step 5: Calculate the molar conductivity Substituting $c_2 = 0.02\,\mathrm{mol\,L^{-1}}$ into the molar-conductivity formula gives

$$\Lambda_{m,2} = \frac{1000\kappa_2}{c_2} = \frac{1000(2.48077 \times 10^{-3})}{0.02} = 124.0385\,\mathrm{S\,cm^2\,mol^{-1}}.$$

The factor 1000 converts the concentration expressed per litre to the corresponding volume in cubic centimetres; it must be included with these units.

Step 6: Conclusion (a) Limiting molar conductivity is molar conductivity at infinite dilution; a fuel cell directly converts the chemical energy of continuously supplied fuel and oxidant into electrical energy. (b) The required conductivity is $\boxed{2.48 \times 10^{-3}\,\Omega^{-1}\,\mathrm{cm^{-1}}}$, and the molar conductivity is $\boxed{124.04\,\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}}$.

Quick Tip to Solve: For the same conductivity cell, first use $\kappa_1 R_1 = \kappa_2 R_2$; then multiply the new conductivity by $1000/c_2$ to obtain molar conductivity.

OR

29(b). (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu.

(b) Calculate emf of the following cell at 298 K:

Mg(s) | Mg^{2+}(0.1 M) || Cu^{2+}(0.01) | Cu(s)

[Given E°_{cell} = +2.71 V, 1 F = 96500 C mol^{-1}] [5 marks]

Solution:

Concept:

- Faraday's first law relates the mass deposited at an electrode to the total charge passed: $m = ZQ = ZIt$, where Z is the electrochemical equivalent, I is current and t is time.
- One faraday is the charge of one mole of electrons: $F = 96500\,\text{C mol}^{-1}$. The electron requirement follows from the balanced electrode reaction.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q_r$, where n is the number of electrons transferred and Q_r is the reaction quotient.

Step 1: (a) State Faraday's first law The mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Thus, for a fixed substance,

$$m \propto Q, \qquad m = ZQ = ZIt.$$

The proportionality constant depends on the substance and its electrode reaction. Hence a larger charge deposits a proportionally larger mass when the same reaction occurs.

Step 2: Find the charge for reduction of copper ions The reduction half-reaction is

$$\text{Cu}^{2+} + 2\text{e}^{-} \longrightarrow \text{Cu}.$$

Each copper ion accepts two electrons, so reduction of $1\,\text{mol}$ of Cu^{2+} requires $2\,\text{mol}$ of electrons. Therefore,

$$Q = 2F = 2(96500) = 193000\,\text{C}.$$

The required charge in terms of faraday is consequently $2F$.

Step 3: (b) Write the cell reaction and reaction quotient Magnesium is oxidised at the anode and copper ions are reduced at the cathode:

$$\text{Mg(s)} \longrightarrow \text{Mg}^{2+}\text{(aq)} + 2e^{-},$$
$$\text{Cu}^{2+}\text{(aq)} + 2e^{-} \longrightarrow \text{Cu(s)}.$$

The overall reaction is $\text{Mg(s)} + \text{Cu}^{2+}\text{(aq)} \longrightarrow \text{Mg}^{2+}\text{(aq)} + \text{Cu(s)}$. Thus $n = 2$. Pure solids have unit activity, so using the stated concentrations,

$$Q_r = \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.1}{0.01} = 10.$$

Quick Tip to Solve: Balance the two electrode reactions first: they give both the two-faraday copper requirement and the value n = 2 in the Nernst equation.

Step 4: Apply the Nernst equation Substitution at 298 K gives

$$E_{\text{cell}} = 2.71 - \frac{0.0591}{2}\log 10$$
$$= 2.71 - 0.02955 = 2.68045\,\text{V}.$$

Since the reaction quotient exceeds unity, the emf is slightly below the standard emf, consistent with the sign of this correction.

Step 5: Conclusion (a) Faraday's first law is $m = ZQ$; the required charge is $2F = 1.93 \times 10^5$ C. (b) The cell emf at 298 K is $\boxed{2.68\,\text{V}}$.

Quick Tip to Solve: Balance the two electrode reactions first: they give both the two-faraday copper requirement and the value n = 2 in the Nernst equation.

30(a). How do you prepare:

(i) K_2MnO_4 from MnO_2?

(ii) $Na_2Cr_2O_7$ from Na_2CrO_4? [2 marks]

Solution:

Concept:

- Potassium manganate contains manganese in oxidation state $+6$; preparing it from MnO_2, which contains Mn(IV), therefore requires oxidation in an alkaline medium.
- Chromate and dichromate ions interconvert according to the acidity of the solution. Addition of acid favours dichromate formation without changing chromium's oxidation state of $+6$.

Step 1: (i) Prepare potassium manganate from manganese dioxide Fuse manganese dioxide with potassium hydroxide in the presence of air or oxygen. The strongly alkaline oxidising conditions convert MnO_2 into green potassium manganate:

$$2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \xrightarrow{\Delta} 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}.$$

Here oxygen acts as the oxidising agent, raising the oxidation state of manganese from $+4$ to $+6$. The product asked for is the green manganate salt.

Step 2: (ii) Prepare sodium dichromate from sodium chromate Acidify an aqueous solution of sodium chromate with sulphuric acid. Yellow chromate is converted to orange dichromate:

$$2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}.$$

The ionic change is

$$2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}.$$

Addition of hydrogen ions shifts this equilibrium towards dichromate; this is an acid-base interconversion rather than a redox reaction.

Step 3: Conclusion (i) Fuse MnO_2 with KOH in air or oxygen to obtain K_2MnO_4. (ii) Acidify

Quick Tip to Solve: Remember the colour sequence: alkaline oxidation produces green manganate, while acidification converts yellow chromate into orange dichromate.

Na_2CrO_4 with H_2SO_4 to obtain $Na_2Cr_2O_7$.

Quick Tip to Solve: Remember the colour sequence: alkaline oxidation produces green manganate, while acidification converts yellow chromate into orange dichromate.

30(b). Account for the following:

(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

(ii) The enthalpy of atomization is lowest for Zn in 3d series of the transition elements.

(iii) Actinoid elements show wide range of oxidation states. [3 marks]

Solution:

Concept:

- Half-filled and completely filled subshells have additional stability; removal of an electron may either destroy or produce such a configuration.
- Enthalpy of atomization measures the energy required to separate a metal into gaseous atoms and therefore reflects metallic bond strength.
- Orbitals of comparable energy can supply different numbers of electrons for chemical bonding.

Step 1: (i) Compare oxidation of manganese(II) and iron(II) The configurations are $Mn^{2+} : [Ar]3d^5$ and $Fe^{2+} : [Ar]3d^6$. Oxidation of Mn^{2+} to Mn^{3+} removes an electron from its especially stable half-filled $3d^5$ subshell and gives $3d^4$. It is therefore relatively difficult. In contrast, oxidation of Fe^{2+} produces $Fe^{3+} : [Ar]3d^5$, gaining half-filled-shell stability. Thus iron(II) is more readily oxidized, whereas manganese(II) is more stable towards oxidation to the +3 state.

Step 2: (ii) Relate zinc's configuration to metallic bonding Zinc has the configuration $[Ar]3d^{10}4s^2$, with a completely filled $3d$ subshell and no unpaired electrons. Its filled $3d$ electrons contribute little to the strong metallic bonding characteristic of the middle members of the series. Consequently, zinc has comparatively weak metal-metal bonding, and the least energy is needed to separate its solid into gaseous atoms. Its enthalpy of atomization is therefore the lowest in the 3d series.

Step 3: (iii) Explain the variable oxidation states of actinoids The $5f$, $6d$ and $7s$ subshells of actinoids have comparable energies. Different numbers of electrons from these subshells can participate in bonding or be removed during compound formation. Since the energy differences are small, several electron-loss possibilities are accessible, giving a wide range of oxidation states, especially among the early actinoids.

Step 4: Conclusion The reasons are: (i) the stable half-filled $3d^5$ configuration of Mn^{2+}, compared with formation of stable $3d^5$ on oxidation of Fe^{2+}; (ii) weak metallic bonding in zinc with its filled $3d^{10}$ subshell; and (iii) comparable energies of actinoid $5f$, $6d$ and $7s$ orbitals.

Quick Tip to Solve: Write the d-electron count before and after oxidation; then check whether half-filled stability is gained or lost.

OR

30(b). (i) Name the element of 3d transition series which shows maximum number of oxidation states. Why does it show so?

(ii) Which transition metal of 3d series has positive $E^\circ(M^{2+}/M)$ value and why?

(iii) Out of Cr^{3+} and Mn^{3+}, which is a stronger oxidizing agent and why?

(iv) Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

(v) Complete the following equation: $MnO_4^- + 8H^+ + 5e^- \rightarrow$ [5 marks]

Solution:

Concept:

- The comparable energies of $3d$ and $4s$ electrons allow transition metals to exhibit several oxidation states.
- The standard reduction potential $E^\circ(\mathrm{M}^{2+}/\mathrm{M})$ depends on the balance of atomization, ionization and hydration energies.
- Half-filled d^5 and f^7 configurations are particularly stable, influencing redox behavior and accessible oxidation states.

Step 1: (i) Identify the element with the most oxidation states Manganese shows the maximum number of oxidation states in the 3d series. Its ground-state configuration is $[Ar]3d^5 4s^2$. It has five unpaired 3d electrons and two 4s electrons, and these subshells are close in energy. Thus different numbers of these seven valence electrons can participate in bonding. Its commonly encountered oxidation states extend from +2 to +7, including +2, +3, +4, +5, +6 and +7.

Step 2: (ii) Explain the positive reduction potential of copper Copper has a positive $E^\circ(\mathrm{Cu}^{2+}/\mathrm{Cu})$, about $+0.34\,\mathrm{V}$. Formation of aqueous Cu^{2+} from metallic copper requires atomization and removal of two electrons. Copper has a high atomization enthalpy and high ionization enthalpies; in particular, the second ionization removes an electron from the stable $3d^{10}$ configuration of Cu^+. The hydration enthalpy of Cu^{2+} does not compensate sufficiently for these energy requirements. Copper is therefore resistant to oxidation to its aqueous divalent ion, and the reverse reduction has a positive standard potential.

Step 3: (iii) Compare chromium(III) and manganese(III) Mn^{3+} is the stronger oxidizing agent. It readily accepts an electron, changing from $3d^4$ to the especially stable half-filled $3d^5$ configuration of Mn^{2+}:

$$\mathrm{Mn}^{3+} + \mathrm{e}^- \longrightarrow \mathrm{Mn}^{2+}.$$

In contrast, Cr^{3+} has a relatively stable $3d^3$ configuration. Reduction to Cr^{2+}, which has $3d^4$, does not gain analogous stability, so chromium(III) has much less tendency to accept an electron.

Step 4: (iv) Give a lanthanoid with a stable +2 state Europium is well known to exhibit the +2 oxidation state. Neutral europium has configuration $[Xe]4f^7 6s^2$; loss of its two 6s electrons gives $\mathrm{Eu}^{2+} : [Xe]4f^7$, whose half-filled 4f subshell stabilizes the divalent state.

Step 5: (v) Complete the acidic permanganate half-reaction In acidic medium, manganese is reduced from +7 in MnO_4^- to +2 and therefore gains five electrons. Four water molecules balance oxygen

Quick Tip to Solve: For redox comparisons, write the configuration of the reduced ion; for half-reactions, check charge as well as atoms.

and eight hydrogen ions balance hydrogen:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O.$$

The left-hand charge is $-1 + 8 - 5 = +2$, equal to the right-hand charge. Both sides contain one manganese atom, four oxygen atoms and eight hydrogen atoms.

Step 6: Conclusion (i) Manganese, because its seven 3d and 4s valence electrons can participate in bonding. (ii) Copper, because hydration does not sufficiently compensate for atomization and ionization. (iii) Mn^{3+}, which reduces to stable $3d^5$. (iv) Europium, with Eu^{2+} having $4f^7$. (v) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$.

Quick Tip to Solve: For redox comparisons, write the configuration of the reduced ion; for half-reactions, check charge as well as atoms.